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GENERAL DYNAMICS

Electric Boat Division
Groton, Connecticut 06340

TRACE CONTAMINANT ANALYSIS FOR SDV SHELTER BREATHING AIR

Swimmer Delivery Vehicle

PREPARED FOR NAVAL SEA SYSTEMS COMMAND,
DEPARTMENT OF THE NAVY, WASHINGTON, DC

By

Sheldon Cohen

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E C Hobaica
E. C. Hobaica, Non-Metallics

Carreau
D. W. Carreau
SDV Shelter Program Manager

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ABSTRACT

A trace contaminant analysis was undertaken in order to determine the toxicity hazard associated with the use of submarine compressed air for SDV shelter breathing. Attention was focused primarily on carbon monoxide, hydrocarbons, and the Freons. The analysis included an evaluation of the following areas:

(a) nature and degree of contamination normally encountered on board submarines,

(b) toxicological effects of the atmospheric constituents,

(c) allowable limits for the contaminants of interest, commensurate with SDV shelter personnel exposure patterns.

Based on the results of the toxicity analysis, it was concluded that compressed submarine atmospheres are safe for use as diver breathing air provided that excess CO_2 and oil mist are removed prior to introduction to breathing manifolds and scuba flasks. Contaminant control equipment can be limited to a CO_2 absorber, an oil mist filter, and to monitoring equipment for carbon monoxide, carbon dioxide, hydrocarbons and Freons.

WHAT ABOUT THE MONITORING of O_2?

Study did not consider influence of elevated levels of O_2 + CO_2 on behavior of contaminant.
i.e. Could thermometabolic or physiological activity create a potential for a synergistic or antagonistic effect on the contaminant?

I. INTRODUCTION

The use of air which has been compressed from the submarine atmosphere for SDV shelter personnel respiratory requirements has raised questions concerning potential toxicity hazards. Within the submarine envelope, a large number of organic and inorganic contaminants are produced from various sources, viz., respiration, smoking, cooking, operating machinery, refrigerant leaks, and off-gassing of solvents from paints, adhesives and sealers. Control of potentially hazardous trace contaminants is accomplished by an air purification and revitalization system comprised of activated charcoal filters, catalytic burners, and an MEA (CO_2) scrubber. Additionally, the use of particularly troublesome substances on board submarines is restricted or prohibited.

and control of
materials Brough
aboard

For this analysis, attention will be focused primarily on total hydrocarbons (aromatic and aliphatic), chlorinated hydrocarbons, Freons and carbon monoxide. The toxicity problems associated with carbon dioxide and oil mists were addressed prior to this study, and appropriate removal systems have been designed into SDV shelter air supply piping.

The aim of this study is to evaluate the need for an additional control and/or monitoring systems required to assure a safe supply of breathing air to SDV shelter personnel. In order to conduct such an evaluation, the following must be determined:

I. (Continued)

(a) The nature and degree of contamination normally encountered on board submarines,

(b) The toxicological effects of the atmosphere constitutents, and

(c) Allowable limits for the contaminants of interest, commensurate with SDV shelter personnel exposure patterns.

II. SDV SHELTER BREATHING AIR PURITY REQUIREMENTS

Current U.S. Navy standards for the purity of diver breathing air and submarine habitability are presented in table 1 for those atmospheric constituents of primary interest. Nuclear submarine habitability standards have been developed and verified over the past 30 years for a large number of potentially hazardous trace contaminants. The levels reflect, in some instances, the production of potentially toxic substances by the ship's air revitalization equipment. BuMed air purity standards for non-saturation (surface-supplied) diving are limited to oxygen, carbon dioxide, carbon monoxide, total hydrocarbons, and oil mist. The levels correspond to a maximum diving depth of 165 feet. The maximum design depth for SDV shelter operations is 200 feet, although depths will not normally exceed 165 feet. It should be noted that the non-saturation diving limit of 25 ppm for total hydrocarbons corresponds to a value of $\sim$100 mg/m^3. This is less restrictive than the 90 day limit for aromatic plus aliphatic hydrocarbons currently in force on submarines.

Industrial Threshold Limit Values (TLV's) have been included in table 1 as additional parameters in the assessment of submarine atmosphere breathability.* TLV's refer to airborne concentrations and represent conditions under which it is believed that nearly all workers may be repeatedly exposed (8 hours/day, 5 days/week) without adverse effect. Except for fast-acting compounds which are controlled by ceiling limits, short-term excursions above the TLV are generally permitted, provided they are compensated by equivalent excursions below the TLV. When used for diving operations at 200 feet, a depth correction of (33 ft/200 ft) must be applied to

* TLVS are not used for SUBMARINE Atmosphere PARAMETERS

TABLE 1

Limits for Atmospheric Constituents, PPM

NOT used for SUBS

	Diving Air		Submarine Atmosphere		
Contaminant	(1) Saturation	Non (2) Saturation	90 Days	24 Hours	TLV
Carbon dioxide	5000	1000	5000	10000	5000
Carbon monoxide	10	20	15	200	50
Methane	1000	–	13000	13000	–
Methanol	200	–	10 (3)	200	200
Total hydrocarbons	10	25	–	–	–
Aliphatics			60 mg/m^3	–	–
Aromatics			10 mg/m^3	–	–
Benzene	1	–	1	100	10
Halocarbons	1	–	–	–	–
Methyl chloroform	–	–	2.5 (3)	10	350
Trichloroethylene	–	–	0.1	–	100
Vinylidene chloride	–	–	2.0	10	10
Freons					
Dichlorodifluoromethane (R-12)	–	–	200 (3)	1000	1000
Dichlorotetrafluorethane (R-114)	–	–	200 (3)	1000	1000
Trichloromonofluoromethane (R-11)	–	–	5 (3)	20	1000
Oil mist	1 mg/m^3	5 mg/m^3	–	–	5

NOTES:

(1) Recommended guidelines are surface equivalent values (NAVMAT P-9290, June, 1976).

(2) Specified in the U.S. Navy Diving Manual for Surface-Supplied Diving Air, June, 1978. Levels corresponds to a maximum depth of 165 feet.

(3) Based on decomposition in CO/H_2 burner.

II. (Continued)

each contaminant TLV to compensate for the effect of increased partial pressure. The effects of increased total pressure, per se, on the complex interaction between toxic substances and normal metabolic processes remain largely unknown, and will be ignored for purposes of this study.

STATEMENT INDICATES THAT TOXICOLOGICAL EFFECTS OF AIRBORNE CONTAM RELATIV. TO HBO CONDITIONS ARE NOT GOING TO BE CONSIDERED

Table 2 summarizes the exposures to submarine compressed air anticipated for SDV shelter personnel during all phases of vehicle launching and recovery. The normal exposure patterns are seen to be less severe than those encountered in industry. As such, TLV's, properly adjusted for diving operations, should provide safety criteria for SDV shelter breathing air purity. In the case of a highly complex mixture of contaminants, such as exists in the submarine atmosphere, the combined effect of the contaminants should be given primary consideration. In the absence of information to the contrary, the effects of the different toxicity hazards should be considered as additive. That is, if the sum of the following fractions: (where C_i = contaminant concentration)

DISAGREE 90day LIMITS Should be USED — PERSONNEL going from SUB TO SDV Should use 90d LIMITS TO ENSURE Safety

$$\frac{C_1}{TLV_1} + \frac{C_2}{TLV_2} + \text{------} \frac{C_n}{TLV_n} = \sum_{i=1}^{n} C_i/TLV_i$$

is greater than one, then the TLV of the mixture is considered to be exceeded.

It should be borne in mind, however, that TLV's are essentially guidelines, and may not be applicable to all exposure conditions. Therefore, it is important to consider also the nature of the contaminant, its inherent chronic or acute toxicity, and length of exposure.

who IS going TO do This? NOT The diver when he HAS A MISSION TO ACCOMPLISH

TABLE 2

SDV Shelter Exposure Patterns

		Normal Exposure(2)		Decompression Treatment
		Time for Each Evolution	Frequency Of Evolution	
Mk VIII Vehicle Launch and Recover	Training(1)	3 hours	2/day, 5 days/ Quarter	-
	Operational Mission	2 hours	1/6 months	-
Mk IX Vehicle Launch and Recover	Training(1)	3 hours	2/day, 5 days/ Quarter	-
	Operational Mission	3 hours	1/6 months	-
Standard Decompression At 165 Feet		-		17 hours
Diving Emergency		-		35 hours

NOTE: (1) Training depth will not normally exceed 70 feet.

(2) Evolution times and frequencies are assumed values.

III. BREATHABILITY OF SUBMARINE ATMOSPHERE

This section consists of an evaluation of the breathability of the submarine compressed air supply for SDV shelter personnel respiratory requirements. Involved is an assessment of contamination levels and associated toxicological effects in the context of a highly complex mixture of atmospheric constituents. The subsequent analysis includes those toxic substances which have been of primary concern to the Navy, viz., aromatic hydrocarbons, chlorinated hydrocarbons and acid gases, and Freons, as well as carbon monoxide.

NOT NRL Ref

DATA IS TOO old TO be TAKEN SERIOUSLY

Information relating to submarine atmosphere contamination during the 1960's and 1970's has been obtained from the results of the Naval Research Laboratory's ongoing atmosphere monitoring program. (1, 2, 3, 4) These contamination levels were then compared to appropriate threshold limit values and submarine 90 days limits in order to ascertain the likelihood of any potential toxicity hazards. In addition, the acute and chronic toxicities of specific compounds were reviewed.

Carbon Monoxide

Carbon monoxide is an odorless, toxic gas whose primary source on board submarines is cigarette smoking. Secondary sources include human metabolism and operating machinery. Cigarette smoking appears to have been declining in recent years. On the average, only one-half of the crew, and one-third of the officers smoke on a regular basis. These proportions may vary significantly from ship to ship.

Where did This come from?

Hemoglobin has an affinity for carbon monoxide 210 times greater than that for oxygen. When carbon monoxide combines with hemoglobin to form carboxy-hemoglobin, HbCO, the capacity of the blood for exchange and transport of oxygen and carbon dioxide is diminished. A condition equivalent to hypoxia is produced. The level of HbCO in the blood slowly approaches an equilibrium value that depends upon the ratio of carbon monoxide to oxygen in the breathing gas. Therefore, the acceptable level of carbon monoxide in the breathing gas is dependent upon the oxygen content instead of the carbon monoxide partial pressure.

what is CO max if 19% O_2?

BuMed's diving air standards limit carbon monoxide to 20 ppm in air containing 20.8% oxygen. At this level, HbCO concentration in the blood will be ~2%, a level below which the first sign of carbon monoxide toxicity will usually occur. According to Sax (1), concentrations of up to 10% HbCO in the blood rarely produce any symptons. Repeated exposures to low concentrations of the gas, up to 100 ppm in air, is generally believed to cause no signs of carbon monoxide poisoning. Daily 8-hour exposure periods of up to 50 ppm carbon monoxide are permitted in industrial situations. Far higher concentrations can be tolerated in emergencies, with varying levels of discomfort. Because carbon monoxide is slow acting, levels up to 200 ppm in air can be tolerated over a 24 hour period, with no significant levels of discomfort.

Table 3 shows carbon monoxide contamination levels in the range of 10-30 ppm for the submarine fleet. For SDV shelter operations under normal and exceptional exposure conditions, these levels will pose no toxicity hazard. It is recommended that the levels of carbon monoxide in the high pressure air supply be monitored so that concentrations higher than 30 ppm can be brought to the attention of SDV shelter personnel.

TABLE 3

Carbon Monoxide - Contamination Levels, PPM, and Toxicity Limits

	Contamination Levels Reported (1)			(2)	Submarine (3)	Toxicity (4)	
	1960	1970	1978	TLV	90 Day Limit	Acute	Chronic
Carbon monoxide	25-30	10-30	10	50	15	High	Slight

Need something more Recent than 1978

(1) Based on data from NRL reports; References 2, 3, 4 and 5.

(2) Industrial Threshold Limit Values (ACGIH), depth adjusted to 200 feet.

(3) NAVSHIPS 0938-011-4010, "Nuclear Powered Submarine Atmosphere Control".

(4) Sax, N.I., "Dangerous Properties of Industrial Materials", 4th Edition.

Hydrocarbons

Organic compounds are the most important class of trace contaminants which are present in the submarine atmosphere. Included in this class are aromatics, aliphatics, olefins, chlorinated hydrocarbons, Freons, and a complex mixture of miscellaneous organics.

These compounds have been quantitatively identified in various NRL reports, (2, 3, 4, 5) the results of which are included in the tables below.

Aromatics, Aliphatics and Olefins

Contamination levels and toxicity information for aromatic, aliphatic and unsaturated hydrocarbons are presented in tables 4, 5, and 6. With the exception of methane, these compounds can be traced to solvents, oils, cements and sealers, as well as to the by-products of smoking, cooking, and decomposition of hot oils. With the exception of the lower hydrocarbons (C_1 - C_5), both the aromatics and higher aliphatics are controlled via oxidation in the ship's catalytic burner and by adsorption onto the main charcoal filter.

The reported contamination levels evidence a distinct trend towards "cleaner" submarines from 1960 through the end of the 1970's. Total hydrocarbon levels have steadily declined from an initial high of 100 mg/m^3 in 1960 (2) to 30 mg/m^3 by 1970 (3), to a low of 10 mg/m^3 by 1978 (5). This dramatic improvement can be attributed to: (a) gradual compliance with regulations restricting painting on board submarines, promulgated in 1965 (6), (b) the prohibition and/or restriction of the use of potentially toxic substances, such as aromatic hydrocarbons, and (c) the upgrading of air revitalization system capabilities and maintenance requirements.

TABLE 4

Aromatic Hydrocarbons - Contamination Levels, PPM, and Toxicity Limits

Compound	Contamination Levels Reported (1)			TLV (2)	Submarine (3)	Toxicity (4)	
	1960	1970	1978	200'	90 Day Limit	Acute	Chronic
* Benzene	0.01	0.02	< 0.1	1.7	1.0	Moderate	High
* Toluene	0.25	0.08	< 0.1	17	10 mg/m^3 (2.5 ppm)	Moderate	Moderate
* Xylene	1.27	0.41	< 0.1	17		Moderate	Moderate
* Ethylbenzene	0.21	0.09	< 0.1	17		Moderate	Moderate
* Propylbenzene	0.04	0.03	< 0.1	-		Moderate	Moderate
* Mesitylene	0.29	0.06	< 0.1	-		High	High
* Ethyl toluene	0.34	-	< 0.1	17		Slight	Moderate
* Pseudocumene	0.57	0.16	< 0.1	-		Moderate	Moderate
* Indane	-	-	< 0.1	-		Unknown	Unknown
$\Sigma C_n/TLV_n$ (5)	0.17	0.06	< 0.05				

(1) Based on data from NRL reports; References (2), (3), (4) and (5).

(2) Industrial Threshold Limit Values (ACGIH), depth adjusted to 200 ft.

(3) NAVSHIPS 0938-011-4010, "Nuclear Powered Submarine Atmosphere Control".

(4) Sax., N.I., "Dangerous Properties of Industrial Materials", 4th Edition.

(5) Relates contaminant levels to TLV of mixture. Assumes effects are additive.

* Prohibited for use on board submarines (NAVSEA 0938-011-4010).

TABLE 5

Aliphatic Hydrocarbons - Contamination Levels, mg/m^3 and Toxicity Limits

Compound	Contamination Levels Reported (1)			*TLV (2)	Submarine (3)	Toxicity (4)	
	1960	1970	1978	mg/m^3	90 Day Limit	Acute	Chronic
Methane	118	0-600	-	-	13,000	Slight	Slight
Ethane	15-80 mg/m^3	20-30 mg/m^3	7-8 mg/m^3	-	60 mg/m^3 (15 ppm)	Moderate	Slight
Butane				240		Moderate	Slight
Pentane				300		Slight	Unknown
Hexane				61		Slight	Slight
Heptane				264		Moderate	Slight
Octane				50		Moderate	Slight
Nonane				242		Moderate	Slight
Undecane						Slight	Slight
Dodicane						Unknown	Unknown
$\sum C_n / TLVn$	< 0.67	< 0.25	< 0.07				

* 200 ft.

(1) Based on data from NRL reports; References (2), (3), (4), and (5).

(2) Industrial Threshold Limit Values (ACGIH), depth adjusted to 200 ft.

(3) NAVSHIPS 0938-011-4010, "Nuclear Powered Submarine Atmosphere Control".

(4) Sax, N.I., "Dangerous Properties of Industrial Materials", 4th Edition.

TABLE 6

Olefins/Alicyclics - Contamination Levels, PPM, and Toxicity Limits

Compound	Contamination Levels Reported (1)			TLV (2) 200'	Submarine (3) 90 Day Limit	Toxicity (4)	
	1960	1970	1978			Acute	Chronic
Acetylene	0.5			-	6000	Moderate	Slight
Ethylene	1.4 - 12.5 mg/m^3	3.0 - 4.0 mg/m^3	1.0 mg/m^3	-	-	Moderate	None
Propylene				-	-	Moderate	None
Butene				-	-	Unknown	Unknown
Isoprene				-	-	Moderate	Unknown
Decene				-	-	Unknown	Unknown
Methyl cyclohexane				66	-	Unknown	High
Ethyl cyclohexane	±			-	-	Unknown	Unknown
$\sum C_n/TLV_n$	< 0.2	< 0.06	0.015				

(1) Based on data from NRL reports; References (2), (3), (4) and (5).

(2) Industrial Threshold Limit Values (ACGIH); depth adjusted to 200 ft.

(3) NAVSHIPS 0938-011-4010, "Nuclear Powered Submarine Atmosphere Control".

(4) Sax, N.I., "Dangerous Properties of Industrial Materials", 4th Edition.

The extremely low levels reported for aromatic hydrocarbons in table 4 are well below both the depth-adjusted TLV's and the 90-day limit. No benzene contamination could be detected.

The atmospheric concentration of aromatics showed a decrease from 17% of the aromatic mixture TLV to less than 5% over the past two decades. Acute and chronic toxicological effects of the aromatic hydrocarbons are generally moderate, with mesitylene and benzene given a high rating. The latter compound is a recognized carcinogen of the blood-forming tissues. Inhalation of xylene and toluene in levels above the TLV may cause impairment of coordination and reaction time.

For the aliphatic hydrocarbons shown in table 5, total contamination levels have dropped from 80 mg/m^3 in 1960 (2) to 8 mg/m^3 in 1978 (3). The latter value is only 7% of the depth-adjusted mixture TLV, and 13% of the 90-day limit. Acute toxicities for the group range from slight to moderate, while chronic toxicities are generally slight. The higher aliphatics may be narcotic in high concentrations.

Table 6 presents a similarily favorable picture for olefins and alicyclics. Both the contamination levels and inherent toxicity are relatively low.

Chlorinated Hydrocarbons

Table 7 shows the chlorinated hydrocarbons which have been quantitatively identified in the submarine atmosphere. Five of the most troublesome compounds, including two common solvents, viz., methyl chloroform and trichloroethylene, have been prohibited or restricted for use on board submarines. These measures have produced extremely low contamination levels of less than 0.1 ppm. This represents less than 15% of the depth-adjusted TLV for the mixture.

The toxicological effects for the group range from slight to high. Methyl chloroform is narcotic in high concentrations. Severe exposure to trichloroethylene can result in cardiac failure. There is also the possibility of liver damage from chronic exposure to trichloroethylene. Methylene chloride and tetrachloroethylene are strong irritants which have an anaesthetic effect at high exposure levels.

The chlorinated hydrocarbons have been particularly troublesome, not only because of their inherent toxicity, but also because some are decomposed and converted to other, more harmful, compounds by shipboard equipment. Table 8 describes the decomposition of four chlorinated hydrocarbons after being passed through the catalytic (H_2 and CO) burner. At normal operating temperatures ($600^{\circ}F$), acid gas (HF, HCl) production predominates. These acid gases are scrubbed by a lithium carbonate filter located downstream of the catalytic burner after-cooler. Methyl chloroform and trichoroethylene yield small amounts of vinylidene chloride (1-3%), a recognized carcinogen.

TABLE 7

Chlorinated Hydrocarbons - Contamination Levels, PPM, and Toxicity Limits

Compound	Contaminated Levels Reported (1)			TLV (2)	Submarine (3)	Toxicity (4)	
	1960	1970	1978	200'	90 Day Limit	Acute	Chronic
Chloroform*	-	-	<0.1 ppm	4.25	-	High	Unknown
Methyl chloroform**	6	-	"	60	2.5	Moderate	Slight
Dichloromethane*	-	-	"	34	-	High	Slight
Carbon tetrachloride *	-	-	"	1.7	-	Slight	High
Vinyl chloride	-	-	"	1.7	-	Moderate	High
Vinlidene chloride	2	-	"	1.7	2.0	Moderate	High
Dichloroethylene	-	-	"	34	-	Slight	Slight
Trichloroethylene *	-	-	"	17	0.1	High	Slight
Tetrachloroethylene *	-	-	"	17	-	Moderate	Moderate
Σ Cn/TLVn			<0.15				

* Prohibited for use on board submarines (NAVSEA 0938-011-4010).

** Restricted to use during construction/overhaul and only with adequate ventilation.

(1) Based on data from NRL reports; References (2), (3), (4) and (5).

(2) Industrial Threshold Limit Values (ACGIH); depth adjusted to 200 ft.

(3) NAVSHIPS 0938-011-4010, "Nuclear Powered Submarine Atmosphere Control".

(4) Sax, N.I., "Dangerous Properties of Industrial Materials", 4th Edition.

TABLE 8

Hopcalite - Catalyzed Decomposition of Chlorinated Hydrocarbons

Compound	% Decomposition @ 600° F	Acid Detected (1)	Decomposition Products @ 600°F		
			Vinylidene Chloride	Trichloroethylene	Tetrachloroethylene
Methyl chloroform	100	15 ppm	2-3%	Trace	-
Trichloroethylene	99	>10 ppm	<1%	-	Trace
Vinylidene chloride	98	25 ppm	-	Trace (2)	-
Tetrachloroethylene	75	10 ppm	-	-	-

(1) Based on an influent concentration of 10 ppm.

(2) At temperatures less than 400°F.

whereas decomposition
it seems to increase

Trichloroethylene is a precursor to dichloroacetylene, an extremely toxic compound (TLV = 0.1 ppm), when passed through a moderately heated alkali scrubber. No problems relating to dichloroacetylene have been reported by the submarine fleet subsequent to relocation of the lithium carbonate FILTER scrubber. With the exception of dichloroacetylene, chlorinated hydrocarbons are readily removed by the ship's activated charcoal filters.

Freons

Table 9 presents data for four Freon refrigerants which have been identified in the submarine atmosphere. R-12 is generally used in the chilled storage refrigeration system, while R-114 is found in the air conditioning plant. R-11 is no longer used on most submarines, and is apparently being phased out. R-113 can only be used on a restricted basis. The use of Freon propellants has also been restricted for use on board submarines.

The toxicity ratings for the Freons for both acute and chronic exposures range from slight to moderate. High concentrations can cause narcosis and anaesthesia.

With reference to table 10, Freons R-12 and R-114 are seen to be highly resistant to Hopcalite-catalyzed decomposition. A substantial percentage of R-11 decomposes when passed through the catalytic burner to yield significant amounts of acid gases (HCl, HF). Freon R-113 shows a slight susceptibility to catalytic oxidation. Any acid gases produced are neutralized by the lithium carbonate filter. No chlorine or phosgene have been detected in the burner effluent for any of the Freons tested.

TABLE 9

Refrigerants (Freons) - Contamination Levels, PPM, and Toxicity Limits

Compound	Contaminated Levels Reported (1)			TLV (2)	Submarine (3)	Toxicity (4)	
	1960	1970	1978	200'	90 Day Limit	Acute	Chronic
Fluorotrichloromethane (R-11)	-	0-15	0-5	170	5	Moderate	Moderate
Dichlorodifluoromethane (R-12)	50	15-50	5-20	170	200	Slight	Slight
Dichlorotetrafluoethane (R-114)	<1	15-50	5-20	170	200	Slight	Unknown
*Trichloroetrifluoroethane (R-113)	-	-	-	170	200	Moderate	Unknown
$\Sigma C_n/TLV_n$		<0.6	<0.24				

* Restricted to use on board limited quantities while in port and only when ventilating outboard.

(1) Based on data from NRL reports; References (2), (3), (4) and (5).

(2) Industrial Threshold Limit Values (ACGIH); depth adjusted to 200 ft.

(3) NAVSHIPS 0938-011-4010, "Nuclear Powered Submarine Atmosphere Control".

(4) Sax, N.I., "Dangerous Properties of Industrial Materials", 4th Edition.

TABLE 10

Resistance of Chlorofluorocarbons to Hopcalite-Catalyzed Decomposition

Compound	Vapor Concentration (ppm)	Loss of Compound, %			Acid Detected, ppm		
		305°C	360°C	415°C	305°C	360°C	415°C
R-11 (CCl_3F)	30-100	17	37	-	5	10	-
R-12 (CCl_2F_2)	420-440	0	0	6	Trace	1-2	5
R-113 ($CClF_2{-}CCl_2F$)	10	1.5	5	26	Trace	-	2.5
R-114 ($CClF_2{-}CClF_2$)	85-410	-	0	0	-	Trace	Trace

Activated charcoal can be useful in controlling Freon contaminant levels. However, if a strict monitoring and/or replacement procedure is not adhered to, the Freons will eventually slowly desorb by displacement with heavier, higher boiling hydrocarbons.

Freon contamination levels in the past have normally ranged from 15 to 50 ppm for R-12 and F-114, and 0 to 15 ppm for R-11 (2). More recent NRL studies (4) indicate a decline to 5 to 20 ppm for R-12 and R-114, and 0 to 5 for R-11. This translates to less than 24% of the depth-adjusted TLV for the Freon mixture shown in table 9. This decline may be attributable, in part, to a more efficient utilization of the main charcoal bed due to: (a) improved charcoal replacement schedules, and (b) much lower overall hydrocarbon contamination with a consequent increase in effective Freon capacity.

Miscellaneous Organics

Some representative and potentially toxic miscellaneous organics are shown in table 11. The ketones, aldehydes, and ethers identified can be traced to paint and cleaning solvents. They are readily oxidized by the catalytic burner and strongly adsorbed by activated charcoal. Any MOST formaldehyde vapor or MEA carry-over from the carbon dioxide scrubber are controlled by the ship's catalytic burner.

TABLE 11

Miscellaneous Organics - Contamination Levels, PPM, and Toxicity Limits

Compound	Reported Contamination Levels (1)			TLV (2)	Submarine (3)	Toxicity (4)	
	1960	1970	1978	200'	90 Day Limit	Acute	Chronic
Acetone	-	-		170	300	Moderate	Slight
Ethanol	-	-	0-2 ppm	170	100	Moderate	Slight
*Methanol	6	-		34	10	Moderate	Moderate
Formaldehyde	-	-		0.34	0.5	High	Slight
Methyl isobutyl ketone	-	-		17	-	High	Unknown
Monoethanolamine	1	-		0.51	0.5	Moderate	Unknown
i-Propyl alcohol	-	-		68	-	Moderate	Slight
Butanol	-	-		8.5	-	Moderate	Slight
Cellosolve	-	-		17	-	Moderate	Slight

* Restricted to use on board submarines in limited quantities while in port and only when ventilating outboard.

(1) Based on data from NRL reports; References (2), (3), (4) and (5).

(2) Industrial Threshold Limit Values (ACGIH); depth adjusted to 200 ft.

(3) NAVSHIPS 0938-011-4010, "Nuclear Powered Submarine Atmosphere Control".

(4) Sax, N.I., "Dangerous Properties of Industrial Materials", 4th Edition.

The most recent data, summarized in table 11, indicates a total concentration for this class of compounds of 0 to 2 ppm, which translated to 0 to 10% of the depth-adjusted TLV for the mixture. Insufficient data have been found with which to evaluate MEA and formaldehyde contamination levels.

Total Hydrocarbons

The foregoing analysis evaluated separately the contamination levels and toxicity hazards for each class of hydrocarbons and found then to be within acceptable limits. The toxicity hazard of the entire mixture of hydrocarbons can be estimated by assuming, in the absence of information to the contrary, that the effects of each group of substances are additive. Table 12 summarizes the additive effects of the hydrocarbon mixture. For those submarine atmospheres analyzed in 1970 (3, 4), the maximum total organic concentration exceeds the TLV of the mixture by ∿10%. It should be noted that the depth-adjusted TLV's include a built-in safety factor of 20%. More recent atmospheric analyses of two candidate host ships show maximum levels equivalent to ∿50% of the total organic mixture TLV. Moreover, the Freons, whose chronic toxicity at low concentrations is rated slight, comprise ∿50% of the total contamination.

In view of the analytical findings cited above, and the levels of cleanliness most recently reported by NRL for submarine atmospheres, it is tentatively concluded that submarine atmospheres are safe for use as sources of diver breathing air, and that no additional equipment is required for removal of hydrocarbon contamination.

How would this conclusion change if the 90d limit is used instead of the TLV

TABLE 12

Total Hydrocarbons - Additive Effects of Hydrocarbon Mixture

	$\Sigma C_n/TLV_n$ (1)		
	1960	1970	1978
Aromatics	0.17	0.06	0.05
Aliphatics	0.67	0.25	0.07
Olefins	0.20	0.06	0.015
Chlorocarbons	-	-	0.15
Freons	-	0.60	0.24
Miscellaneous	-	-	-
$\Sigma\Sigma C_n/TLV_n$		1.12	0.52

(1) Relates atmospheric contamination levels to TLV of mixture. Assumes effects are additive.

IV. PROPOSED TRACE CONTAMINANT CONTROL SYSTEM

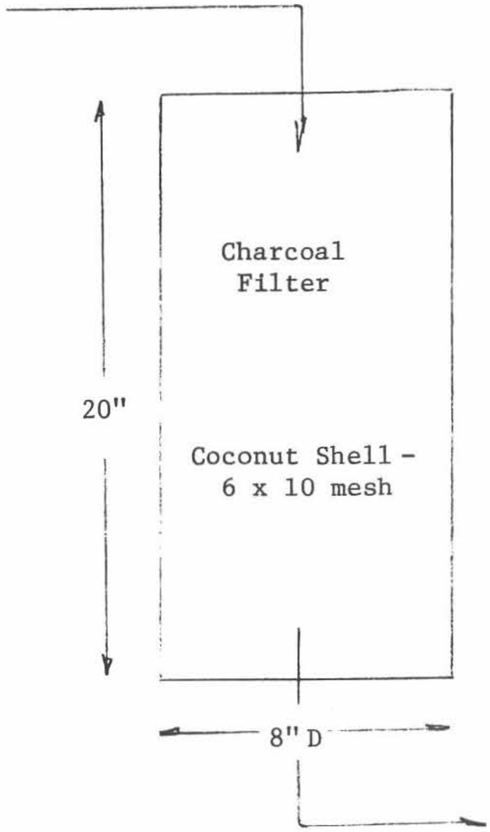
Based on the results of the foregoing toxicity analysis of submarine atmospheres, the inclusion of a contaminant removal system for the control of carbon monoxide and hydrocarbons including the Freons, does not appear to be warranted. However, provisions for contaminant monitoring should be included in the high pressure air delivery system. This will be elaborated upon at a later juncture. Should the installation of a contaminant removal system be contemplated to assure acceptable air quality under any or all circumstances, specific recommendations concerning the advantages and drawbacks of several filter materials are discussed below.

Apart from carbon monoxide, and acid gases which will be removed by a carbon dioxide scrubber, virtually all of the potentially hazardous atmospheric constituents are organic compounds which are condensable at, or close to, ambient temperatures. Hence, the use of an activated charcoal filter should result in effective control of trace hydrocarbon contamination, especially at high pressures where equilibrium conditions are more favorable. Operation at low humidities will further enhance both adsorption efficiency and capacity.

A summary of the preliminary design characteristics of a vertical charcoal bed, encased in a housing similar to that of the carbon dioxide adsorber presently being constructed for the SDV shelter air supply, is presented in figure 1.

FIGURE 1

Proposed Charcoal Filter Design



DESIGN CHARACTERISTICS

1. Vertical Bed: 8" dia. x 20" L.

2. Temperature = Ambient
Pressure = 300 - 3000 psi
Relative Humidity = 10%

3. Bed Volume = $0.5\ ft^3$
Weight of Charcoal = 14 lbs.
Superficial Velocity = 1.5 - 14 fpm

4. *Minimum Bed Capacity = 17.5%
**Minimum Time to Bed Exhaustion = 20 hours

* Based on estimated effective capacity for mixture of hydrocarbons and Freons at 300 psi and 25°C.

** Based on air flow of 105 scfm and a total hydrocarbon contamination of 60 ppm.

Air should flow upward to reduce particle carryover and reduce channeling.

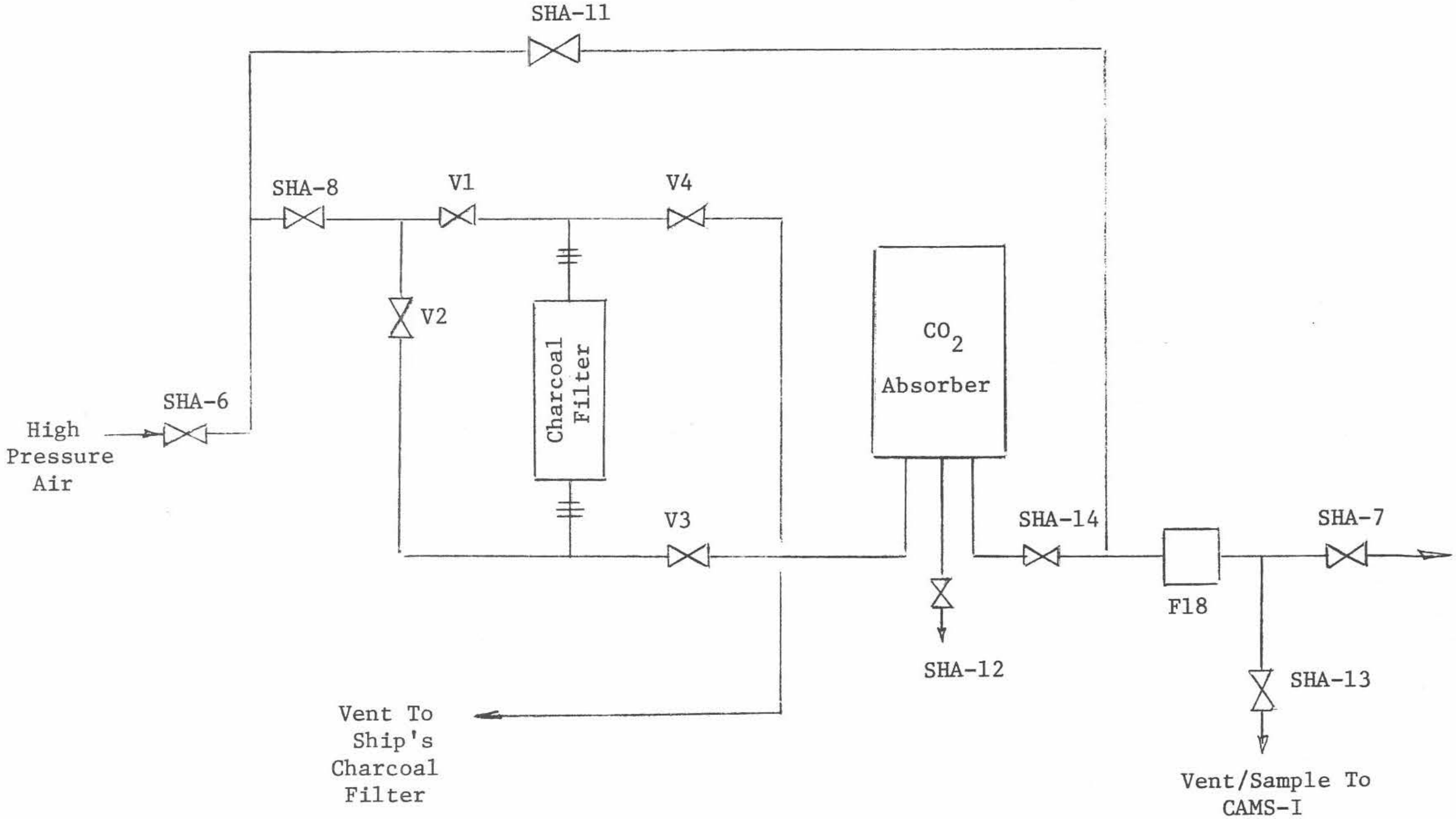
Undesirable and potentially hazardous effects can occur, however, whenever there is a large decrease in partial pressures of the trace contaminant gases. "Slugs" of contaminants adsorbed at relatively high partial pressures will be desorbed when the partial pressures are lowered substantially and will be redistributed throughout the bed adsorption zone. Should this occur as bed saturation is approached, the release of all "excess" hydrocarbons adsorbed at the higher partial pressures will result. This desorption effect can be produced by a shift from high to low operating pressure. In this case, the release will be fairly rapid, and can produce transient spikes in hydrocarbon contamination levels of from 100 to 200 ppm or higher. A large release of carbon dioxide, at concentration up to 5%, can also occur. Desorption can also be effected by switching to a "cleaner" air bank; in this case, the release rate should be relatively slow and the resultant increase in contamination levels minimal.

The undesirable desorption effects discussed above can be circumvented. Each adsorption period at high pressure should be followed by venting in an upflow (counterflow) direction, during depressurization, through the ship's carbon filter to the main fan room, as shown in figure 2. Based on a one-hour charging period at 3000 psi, each venting will release less than 0.1 lb of hydrocarbons and Freon to the ship's main charcoal filter. The simultaneous release of adsorbed carbon dioxide to the main fan room can increase the ship's carbon dioxide concentration by 100 ppm.

TOO SMALL TO MATTER

FIGURE 2

Recommended Installation of a Proposed Contaminant Control System



The use of a Purafil filter, an activated alumina adsorbent impregnated with potassium permangenate, is not recommended for this application. Although useful for the control of many organic and inorganic compounds, Purafil will not effectively remove Freons or aliphatic hydrocarbons.

It is recommended that provisions for sampling and analysis be incorporated into the contaminant control system for monitoring trace contaminant levels as well as the effectiveness of the carbon dioxide scrubber and charcoal filter.

Most of today's submarines, including the candidate host ships are equipped with CAMS-I (Central Atmosphere Monitoring System) units. These analytical devices consist of an infrared spectrometer to monitor carbon monoxide, coupled with a fixed collector mass spectormeter to monitor hydrogen, nitrogen, carbon dioxide, oxygen, water, and Freons R-11, R-12 and R-114.

CAMS-II prototypes, which are also capable of detecting the different classes of hydrocarbons, are currently under evaluation at NRL. An OPEVAL is scheduled for 1982. In the interim, a portable Trace Gas Analyzer can be made available by NRL for monitoring total hydrocarbon concentrations.

The CAMS-I unit samples the atmosphere at various pre-selected locations throughout the submarine via the positioning of a manual selector valve. It is recommended that a gas line be installed running from the CAMS-I selector valve to vent/sample valve SHA-13 downstream of the CO_2 adsorber. Proposed guidelines for monitoring trace contaminants in the SDV shelter breathing air supply are listed in table 13, along with

AIR MUST BE @
ATM PSI IN order
NOT TO damage
CAMS

IV. (Continued)

corresponding submarine 90-day limits. Should one or more of the contaminants under surveillance be out of tolerance, a judgement as to the safety of the breathing air can be made, and appropriate measures taken.

By who?
what guidelines!

TABLE 13

Proposed Guidelines for Monitoring of Trace Contaminants

	Recommended SDV Shelter Limit, ppm	Submarine 90 Day Limit, ppm
	Thalmann	
Carbon monoxide	30 ← 20	15
Freons		
R-11	15	5 *
R-12	50	200
R-114	50	200
Total hydrocarbons	40 mg/m^3	100 mg/m^3
Carbon dioxide	850	5000

* Based on decomposition in the ship's catalytic (CO/H_2) burner.

V. CONCLUSIONS

1. Based on an assessment of contamination levels encountered on board submarines, and associated toxicological effects, compressed submarine atmospheres are considered safe for use as diver breathing air, provided carbon dioxide and oil mist contamination are effectively removed.

2. The inclusion of contaminant removal equipment for the control of carbon monoxide, hydrocarbons, and the Freons appears to be unnecessary.

3. For SDV shelter operations under normal and exceptional exposure conditions, carbon monoxide will pose no toxicity hazard.

4. Hydrocarbon contamination levels reported over the past decade, when considered separately and as a total mixture, remain well below depth-adjusted limit values recommended to ensure breathing air purity.

5. The Freon levels identified in the submarine atmosphere do not represent a toxicological problem in terms of SDV shelter respiratory requirements. Any halogen acids produced as a result of decomposition in the catalytic burner will be removed by the lithium carbonate filter of the carbon dioxide adsorber.

VI. RECOMMENDATIONS

1. ✓ Provisions for sampling and analysis should be incorporated into the proposed contaminant control system for monitoring trace contaminant levels, as well as the effectiveness of the carbon dioxide adsorber and charcoal filter.

2. ✓ It is recommended that the vent/sample valve SHA-13 downstream of the carbon dioxide adsorber be connected to the ship's CAMS-I selector valve for the monitoring of CO_2, CO, and Freons R-11, R-12 and R-114.

3. ✓ Total hydrocarbon concentrations should be monitored by the ship's Total Hydrocarbons Analyzer (THA). In the absence of an operational THA, a portable Trace Gas Analyzer (TGA) should be obtained from NRL.

4. Should the inclusion of a hydrocarbon filter be contemplated, the use of activated charcoal is recommended. However, specific installation and operating guidelines must be followed. The use of a Purafil filter in the host ship is not recommended.

BUMED Review

VII. REFERENCES

1. Sax, N.I., "Dangerous Properties of Industrial Materials", 4th Edition.

2. Carhart, H.W., & Piatt, V.R., "Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines", 3rd Annual NRL Progress Report, dated 12/63.

3. Carhart, H.W., & Thompson, J.K., "Removal of Contaminants from Submarine Atmospheres, ACS Symposium, dated 1975.

4. Sealfield, H.W., & Wyatt, J.R., "NRL's Central Atmosphere Monitor Program", NRL Report, dated 12/76.

5. Unpublished Study conducted by NRL (Wyatt) in 1978.

6. NAVSEA 0938-011-4010, Appendix B, "Nuclear Powered Submarine Atmosphere Control".